The Kinetic Theory of Simple and Composite Monatomic Gases : Viscosity, Thermal Conduction, and Diffusion.

By S. CHAPMAN, M.A., D.Sc., Fellow and Lecturer of Trinity College, Cambridge.

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(Abstract.*)

INTRODUCTION.

The mean-free-path phenomena of gases can be explained in a general way by a very elementary form of the kinetic theory, but to develop a satisfactory mathematical treatment of them, yielding accurate numerical results, is less easy. The difficulty varies to some extent with the nature of the molecular model chosen as basis. It is curious that the adoption of one particular model, viz., a centre of force varying inversely as the fifth power of the distance, removes nearly all the analytical complications in the theory. The first accurate treatment of viscosity, conduction, and diffusion, due to Maxwell, was made possible by this fact, and it is remarkable that Maxwell's theory requires no knowledge of the velocity-distribution function corresponding to the non-uniform state of the gas. If the molecules are of any

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* This abstract summarises two papers in the 'Philosophical Transactions,' the first (received October 5, 1915) dealing with simple gases ('Phil. Trans.,' A, vol. 216, pp. 279–348, 1915), and the second (received May 19, 1916) with composite gases. These two papers amplify and complete an earlier memoir ('Phil. Trans.,' A, vol. 211, pp. 433–483 (1911)), which contains a first approximation to the present theory.

other type, the function must be determined, a task wherein lies the main difficulty of the investigation. It is, however, of more than mathematical interest to widen the basis of the theory, since Maxwell's molecular model does not satisfactorily represent the molecules of actual gases.

The velocity-distribution function has been proved by Boltzmann to satisfy a certain integral equation, which Hilbert has shown to be sufficient to determine the function uniquely. Lorentz has solved an important degenerate form of this equation, while Pidduck* has obtained solutions of some typical examples of the general case, and so deduced many interesting numerical results relating to diffusion. The present method, however, is not based on Boltzmann's equation. Though less direct, it seems to possess advantages not shared by the other method, in that it yields results of complete formal generality, which can be reduced to numerical form with comparatively little arithmetical labour. To comply with the requirements of the pure mathematician, the results should be proved to be in conformity with Boltzmann's equation. Progress has already been made in this direction, and has brought to light several theorems of much analytical interest. As the insertion of these would be unsuitable in memoirs intended primarily to deal with questions of physics, they are reserved for a future paper.

PART I.—OUTLINE OF THE MATHEMATICAL METHOD.

(1) *Notation and Analysis of the State of the Gas.*

We consider a gas composed of a mixture of two sets of spherically symmetrical molecules of masses m_1, m_2,† in numbers ν_1, ν_2 per unit volume at (x, y, z, t).‡ The component densities ρ_1, ρ_2, are consequently equal to $\nu_1 m_1$, $\nu_2 m_2$. The external force acting on each molecule m_1 (and similarly for the molecules m_2, with change of suffix throughout) will be denoted by (X_1, Y_1, Z_1), or, vectorially, by P, while the mean velocity of this group of molecules at (x, y, z, t) will be denoted by (u_1, v_1, w_1) or vectorially by c_1. The proportions of either kind of gas will be denoted by λ_1, λ_2, so that

$$\lambda_1 = \nu_1/\nu_0, \qquad \lambda_2 = \nu_2/\nu_0,$$

where $\nu_0 = \nu_1 + \nu_2$; evidently $\lambda_1 + \lambda_2 = 1$.

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* Boltzmann, 'Vorlesungen über Gastheorie,' vol. 1, p. 114; Hilbert, 'Math. Ann. (1912); Lorentz, 'Theory of Electrons,' p. 268; Pidduck, 'Proc. Lond. Math. Soc., (2), vol. 15, p. 89 (1915). Also *cf.* Lunn, 'Bull. Amer. Math. Soc.,' vol. 19, p. 455 (1913); Enskog, 'Phys. Zeit.,' vol. 12, p. 58 (1911).

† For convenience we shall suppose the heavier gas to be taken as gas (1), so that $m_1 > m_2$.

‡ *I.e.*, at the point (x, y, z), and at time t.

The suffix 0 here, and throughout, refers to the composite gas as a whole. Thus the mean mass m_0, or external force P_0 (or X_0, Y_0, Z_0) per molecule, and the mean velocity c_0 (or u_0, v_0, w_0) of the gas as a whole, are given by equations of the type

$$m_0 = \lambda_1 m_1 + \lambda_2 m_2, \qquad X_0 = \lambda_1 X_1 + \lambda_2 X_2,$$

and so on. Evidently, the total density ρ_0, equal to $\rho_1 + \rho_2$, is also given by $\nu_0 m_0$.

The suffix 0, together with a dash ('), will relate to certain multiples of the difference between the values of various data for the component gases.

Thus we define λ_0', m_0', ρ_0', P_0', c_0' by the equations

$$2\lambda_0' = \lambda_1 - \lambda_2, \quad m_0' = \lambda_1 \lambda_2 (m_1 - m_2), \quad \rho_0' = \nu_0 m_0'/\lambda_1 \lambda_2 = \nu_0 (m_1 - m_2),$$

$$P_0' = \lambda_1 \lambda_2 (m_2 P_1/m_0 - m_1 P_2/m_0), \quad c_0' = \lambda_1 \lambda_2 (c_1 - c_2).$$

By inverting the above equations, we obtain the following expressions for the original quantities m_1, P_1, etc., in terms of m_0, m_0', P_0, and so on :—

$$m_1 = m_0 + m_0'/\lambda_1, \qquad P_1 = m_1 P_0/m_0 + P_0'/\lambda_1, \qquad c_1 = c_0 + c_0'/\lambda_1,$$

$$m_2 = m_0 - m_0'/\lambda_1, \qquad P_2 = m_2 P_0/m_0 - P_0'/\lambda_2, \qquad c_2 = c_0 - c_0'/\lambda_2.$$

It may readily be seen that the motion of the gas can be analysed into (*a*) a steady motion of the gas as a whole with velocity c_0, together with (*b*) a motion of interdiffusion in which equal numbers ($\nu_0 c_0'$ per second) of the two groups of molecules are transported in opposite directions, the mean velocities of the two streams being c_0'/λ_1 and $-c_0'/\lambda_2$. The momentum of the common motion (*a*) is $\rho_0 c_0$, while the resultant momentum of the motion of interdiffusion (due to the difference of molecular mass) is $\rho_0' c_0'$; it is easily seen that, with the above definitions,

$$\rho_1 c_1 + \rho_2 c_2 = \rho_0 c_0 + \rho_0' c_0'.$$

As regards the resolution of the forces into multiples of P_0 and P_0', the first terms, $m_1 P_0/m_0$ on m_1 and $m_2 P_0/m_0$ on m_2, represent forces which will impart a common acceleration P_0/m_0 to each group of molecules (we may suppose this to modify the common stream-velocity c_0). The remaining components of P_1 and P_2, when summed up over the ν_1 or ν_2 molecules of the corresponding group, afford equal and opposite total forces $\pm \nu_0 P_0'$; such interdiffusing groups of molecules as we consider in (*b*) will exert equal and opposite forces on one another, and the forces acting on the two groups must be equal and opposite if the motion of interdiffusion is to be maintained, or modified without imparting any common velocity to them. As for λ_0', it is introduced for the sake of symmetry: D denoting any differential operator, clearly

$$D\lambda_1 = -D\lambda_2 = \tfrac{1}{2} D(\lambda_1 - \lambda_2) = D\lambda_0'.$$

We next consider the motions of individual molecules. The velocity of a typical molecule m_1 will be denoted by $(u)_1$, $(v)_1$, $(w)_1$, or $(c)_1$, when referred to the co-ordinate axes, or when referred to axes moving with the velocity c_0 appropriate to the given values of (x, y, z, t), by U_1, V_1, W_1 or C_1. Thus,

$$C_1 = (c)_1 - c_0, \qquad C_2 = (c)_2 - c_0,$$

the second equation referring to the molecules m_2.

The mean value of any function of the molecular velocities will be denoted by a bar placed above the expression for the function. Hence, by definition,

$$\overline{(c)_1} = c_0 + \overline{C_1} = c_1, \qquad \overline{(c)_2} = c_0 + \overline{C_2} = c_2,$$

or

$$\overline{C_1} = c_1 - c_0 = c_0'/\lambda_1, \qquad \overline{C_2} = c_2 - c_0 = -c_0'/\lambda_2.$$

So far, C has denoted a vector quantity, and the equations involving it have been vectorial: henceforward it will denote the amplitude of the vector, so that C is essentially positive, and

$$C_1{}^2 = U_1{}^2 + V_1{}^2 + W_1{}^2, \qquad C_2{}^2 = U_2{}^2 + V_2{}^2 + W_2{}^2.$$

The mean energy of the motion (U, V, W) " peculiar " to each molecule is clearly $\frac{1}{2}m\overline{C^2}$ per molecule, and we write

$$m_1\overline{C_1{}^2} = 3/2h_1 = 3RT_1, \qquad m_2\overline{C_2{}^2} = 3/2h_2 = 3RT_2,$$

where R is the universal gas-constant. These equations define h and T; T_1, T_2, will be termed the " temperatures " of the component gases, which are not necessarily exactly equal, though all the departures of the gas from the uniform state will be supposed small. The mean hydrostatic pressures of the component and composite gases, and also h_0 and T_0 (the " temperature" of the composite gas) are defined by

$$p_1 = \tfrac{1}{3}\nu_1 m_1 \overline{C_1{}^2} = \nu_1/2h_1 = R\nu_1 T_1, \quad p_2 = \tfrac{1}{3}\nu_2 m_2 \overline{C_2{}^2} = \nu_2/2h_2 = R\nu_2 T_2,$$

$$p_0 = p_1 + p_2 = \nu_1/2h_1 + \nu_2/2h_2 = \nu_0/2h_0 = R\nu_0 T_0.$$

Clearly $\qquad T_0 = \lambda_1 T_1 + \lambda_2 T_2, \qquad 1/h_0 = \lambda_1/h_1 + \lambda_2/h_2.$

The six pressure components p_{xx}, p_{yy}, p_{zz}, p_{xy}, p_{yz}, p_{zx}, for the component and composite gases are similarly defined, *e.g.*,

$$(p_{xx})_0 = (p_{xx})_1 + (p_{xx})_2 = \nu_1 m_1 \overline{U_1{}^2} + \nu_2 m_2 \overline{U_2{}^2},$$

$$(p_{xy})_0 = (p_{xy})_1 + (p_{xy})_2 = \nu_1 m_1 \overline{U_1 V_1} + \nu_2 m_2 \overline{U_2 V_2}.$$

We also define T_0', p_0', h_0', by the equations

$$T_0' = \lambda_1 \lambda_2 (T_1 - T_2), \qquad 1/h_0' = \lambda_1 \lambda_2 (1/h_1 - 1/h_2)$$

$$p_0' = \nu_0/2h_0' = \lambda_1 \lambda_2 (p_1/\lambda_1 - p_2/\lambda_2) = R\nu_0 T_0'.$$

Evidently $\qquad T_1 = T_0 + T_0'/\lambda', \qquad T_2 = T_0 - T_0'/\lambda_2,$

and T_0' is a measure of the difference between the temperatures of the component gases.

(2) *The Velocity-Distribution Function.*

When the gas is uniform, so that c_0, λ, h_0 are constant, while c_0', h_0', P, are zero, the function $f(U, V, W)$ representing the distribution of the components of velocity (U, V, W) among the molecules m_1 or m_2 assumes Maxwell's well known form:

$$[f_1(U_1, V_1, W_1)]_0 = (h_0 m_1/\pi)^{3/2} e^{-h_0 m_1 C_1^2},$$

$$[f_2(U_2, V_2, W_2)]_0 = (h_0 m_2/\pi)^{3/2} e^{-h_0 m_2 C_2^2}.$$

These clearly satisfy the necessary conditions

$$\iiint f(U, V, W)\, dU\, dV\, dW = 1, \qquad \iiint f(U, V, W)\, C^2\, dU\, dV\, dW = 3/2\, hm.$$

For the velocity distribution function in the slightly disturbed state we shall write

$$f_1(U_1, V_1, W_1) = [f_1]_0\, [1 - \phi_1(U_1, V_1, W_1)],$$

where ϕ_1 is a function, of the first order of smallness, which remains to be determined.

(3) *The Equations of Transfer.*

Let Q_1 be any function of the velocity components $(u)_1$, $(v)_1$, $(w)_1$, of a molecule m_1; then $\nu_1 \overline{Q_1}$ is the aggregate value of Q_1 summed over all the molecules in unit volume. The equation expressing the analysis of the rate of change of $\nu_1 \overline{Q_1}$ is called the "equation of transfer" of Q_1. It may readily be shown to be[*]

$$\frac{\partial}{\partial t}(\nu_1 \overline{Q_1}) = \Delta Q_1 - \sum_{x, y, z}\left[\frac{\partial}{\partial x}(\nu_1 \overline{(u)_1 Q_1}) - \frac{\nu_1}{m_1} X_1 \overline{\left(\frac{\partial Q_1}{\partial (u)_1}\right)}\right].$$

The rate of change is here analysed into (a) the part ΔQ_1 due to the encounters between the molecules m_1 among themselves or with the others m_2, (b) the part due to the passage of molecules into or out of the volume considered, and (3) that caused by the action of external forces.

By assigning to Q the values unity, (u), or $(c)^2$, we may obtain the equations of continuity, momentum, or energy, for the composite gas, since in these three cases, by virtue of the conservation of mass, momentum, and energy, we may eliminate ΔQ.

Three special functions Q are important in the present theory. By means of the three equations just mentioned, and by the neglect of all second-order

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[*] *Cf.* Jeans' 'Dynamical Theory of Gases,' § 335 (2nd ed.).

quantities, the corresponding equations of transfer may be reduced to the following form:—

$$\frac{3 \, (2h_0 m_1)^s}{1 \cdot 3 \dots (2s+3)} \, m_1 \Delta U_1 C_1^{2s} = \nu_0 \xi_0' + R s \nu_1 \frac{\partial T_0}{\partial x},$$

$$\frac{3 \, (2h_0 m_2)^s}{1 \cdot 3 \dots (2s+3)} \, m_2 \Delta U_2 C_2^{2s} = - \nu_0 \xi_0' + R s \nu_2 \frac{\partial T_0}{\partial x},$$

$$\frac{(2h_0 m_1)^s}{1 \cdot 3 \dots (2s+1)} \Delta C_1^{2s} = \nu_0 \frac{\partial \lambda_0'}{\partial t} = - \frac{(2h_0 m_2)^s}{1 \cdot 3 \dots (2s+1)} \cdot \Delta C_2^{2s}$$

$$\frac{3 \, (2h_0 m_1)^{s+1}}{1 \cdot 3 \dots (2s+3)} \Delta U_1^2 C_1^{2s} = \nu_0 \frac{\partial \lambda_0'}{\partial t} + \frac{2}{15} \, (2s+5) \, \nu_1 c_{xx},$$

$$\frac{3 \, (2h_0 m_2)^{s+1}}{1 \cdot 3 \dots (2s+3)} \Delta U_2^2 C_2^{2s} = - \nu_0 \frac{\partial \lambda_0'}{\partial t} + \frac{2}{15} \, (2s+5) \, \nu_2 c_{xx},$$

$$\frac{3 \, (2h_0 m_1)^{s+1}}{1 \cdot 3 \dots (2s+3)} \frac{1}{\nu_1} \Delta V_1 W_1 C_1^{2s} = \frac{2}{15} \, (2s+5) \, c_{yz} = \frac{3 \, (2h_0 m_2)^{s+1}}{1 \cdot 3 \dots (2s+3)} \frac{1}{\nu_2} \Delta V_2 W_2 C_2^{2s}.$$

The following equations define ξ_0', c_{xx}, c_{xy}, and there are, of course, similar quantities η_0', ζ_0', c_{yy}, and so on, which are defined in like manner :

$$\xi_0' = \frac{1}{2h_0} \frac{\partial \lambda_0'}{\partial x} - X_0' - \frac{m_0'}{\nu_0 m_0} \frac{\partial p_0}{\partial x},$$

$$c_{xx} = 2 \partial u_0 / \partial x - \partial v_0 / \partial y - \partial w_0 / \partial z, \qquad c_{yz} = \tfrac{3}{2} \, (\partial v_0 / \partial z + \partial w_0 / \partial y).$$

In each of the above equations of transfer, as written, a multiple of ΔQ is equated to certain " external " or mean data of the gas. The reduction to this form requires no knowledge of the small deviation from Maxwell's distribution law of molecular velocities, *i.e.*, of the function $\phi (U, V, W)$, but such knowledge is necessary for the calculation of ΔQ. Conversely, however, the above equations for ΔQ throw light on the form of $\phi (U, V, W)$; in fact, if we assume that ϕ can be expressed as a power series in U, V, W, we may in this way[*] infer that it will have the following form :—

$$\phi_1 (U_1, V_1 W_1) = \tfrac{1}{3} 2h_0 m_1 A_0 (U_1 \xi_0' + V_1 \eta_0' + W_1 \zeta_0') F_1 (C_1^2)$$

$$+ \tfrac{1}{3} 2h_0 m_1 B_0 (U_1 \partial T_0 / \partial x + V_1 \partial T_0 / \partial y + W_1 \partial T_0 / \partial z) G_1 (C_1^2)$$

$$+ \tfrac{2}{45} 2h_0 m_1 C_0 (c_{xx} U_1^2 + \dots + 2c_{yz} V_1 W_1 + \dots) H_1 (C_1^2) + D_0 \, \partial \lambda_0' / \partial t \cdot J_1 (C_1^2).$$

The function ϕ_2 is obtainable by changing the suffix 1 into 2 throughout. We express the functions $F (C^2)$, etc., in power series which are conveniently written as follows:—

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[*] The details of the deduction will be found in the original papers, where it is shown how ΔQ depends on $\phi (U, V, W)$.

$$F_1(C_1{}^2) = \sum_{r=0}^{\infty} \alpha_r \frac{(2h_0 m_1)^r}{1 . 3 \dots (2r+3)} C_1{}^{2r}, \qquad G_1(C_1{}^2) = \sum_{r=0}^{\infty}{}' \beta_r \frac{(2h_0 m_1)^r}{1 . 3 \dots (2r+3) r} C_1{}^{2r},$$

$$H_1(C_1{}^2) = \sum_{r=0}^{\infty} \gamma_r \frac{(2h_0 m_1)^r}{1 . 3 \dots (2r+5)} C_1{}^{2r}, \qquad J_1(C_1{}^2) = \sum_{r=0}^{\infty} \delta_r \frac{(2h_0 m_1)^r}{1 . 3 \dots (2r+1)} C_1{}^{2r}.$$

The dash ($'$) after the sign of summation in $G(C^2)$ is to indicate that r is to be omitted from the numerical factor of the first term ($r = 0$). These factors are arbitrary and not really necessary, since the coefficients $\alpha, \beta, \gamma, \delta$ are unknown, but their insertion is analytically advantageous. Similarly it is convenient to denote the coefficients in $F_2(C_2{}^2)$, etc. (which expressions correspond to $F_1(C_1{}^2)$, etc., apart from the natural change of suffix) by $\alpha_{-r}, \beta_{-r}, \gamma_{-r}, \delta_{-r}$; it is then necessary to distinguish between α_r and α_{-r}, and so on, even when $r = 0$.

The factors A_0, B_0, C_0, D_0, in ϕ can be chosen at will, after which the coefficients $\alpha, \beta, \gamma, \delta$, become definite; these remain to be determined. Certain relations between them, however, hold good, in virtue of the conditions

$$\iiint f(U, V, W) \, dU \, dV \, dW = 1, \quad \iiint f(U, V, W) C^2 \, dU \, dV \, dW = 3/2hm,$$

$$\iiint f(U, V, W) U \, dU \, dV \, dW = u - u_0,$$

which (with the proper suffixes appended) $f_1(U_1, V_1, W_1)$ and $f_2(U_2, V_2, W_2)$ must clearly satisfy. These are readily seen to yield the equations :

$$\sum_{r=0}^{\infty} \delta_r = \sum_{r=0}^{\infty} \delta_{-r} = 0,$$

$$\lambda_1 \sum_{r=0}^{\infty} (2r+3) \delta_r = -\lambda_2 \sum_{r=0}^{\infty} (2r+3) \delta_{-r} = -3 T_0'/D_0 (\partial \lambda_0'/\partial t),$$

$$\tfrac{1}{9} \lambda_1 \{ A_0 \xi_0' \sum_0^{\infty} \alpha_r + B_0 (\partial T_0/\partial x) \sum_{r=1}^{\infty}{}' r^{-1} \beta_r \}$$

$$= -\tfrac{1}{9} \lambda_2 \{ A_0 \xi_0' \sum_{r=0}^{\infty} \alpha_{-r} + B_0 (\partial T_0/\partial x) \sum_{r=0}^{\infty}{}' r^{-1} \beta_r \} = -u_0'.$$

In the last equation, ξ_0' and $\partial T_0/\partial x$ are entirely independent quantities ; hence, if we eliminate u_0', we can separately equate their co-factors to zero, in the resulting equation. In this way the above equations may be re-written

$$\lambda_1 \sum_0^{\infty} \alpha_r = -\lambda_2 \sum_0^{\infty} \alpha_{-r} \equiv -\alpha_0',$$

$$\lambda_1 \sum_0^{\infty}{}' r^{-1} \beta_r = -\lambda_2 \sum_0^{\infty}{}' r^{-1} \beta_{-r} \equiv -\beta_0',$$

$$2\lambda_1 \sum_1^{\infty} r \delta_r = -2\lambda_2 \sum_1^{\infty} r \delta_{-r} \equiv -\delta_0',$$

which also define α_0', β_0', and δ_0' ; consequently, also

$$u_0' = \tfrac{1}{9}\left(\alpha_0'\,A_0\,\xi_0' + \beta_0'\,B_0\,\partial T_0/\partial x\right),$$
$$T_0' = \tfrac{1}{9}\delta_0'\,D_0 T_0\,\partial\lambda_0'/\partial t.$$

(4) *Determination of the Coefficients* α, β, γ, ∂.

By means of the above expression for $f\,(\mathrm{U},\ \mathrm{V},\ \mathrm{W})$ it is possible to calculate $\Delta\,\mathrm{Q}$, the operation (a lengthy and elaborate one) consisting in the evaluation of an octuple integral involving the eight variables which are required to specify an encounter between two molecules. Small quantities of order higher than the first are neglected, and the resulting expression for $\Delta\,\mathrm{Q}$ always consists of a linear series of the coefficients $\alpha_r, \beta_r, \gamma_r, \delta_r,$ multiplied respectively into ξ_0', $\partial T_0/\partial x, c_{xx}, \partial\lambda_0'/\partial t$, etc.; the factor of each term in these linear series depends only on ν, h_0, and m, and involves the law of molecular interaction during encounter. It is found possible to obtain perfectly general expressions for these factors, *i.e.*, no particular law of interaction has to be assumed.

On inserting the values of ΔQ, so calculated, in the above equations of transfer, we may separately equate the parts on the two sides which contain ξ_0', $\partial T_0/\partial x$, c_{xx}, or $\partial\lambda_0'/\partial t$. We thus obtain a number of equations, each of which is linear in one set only of the coefficients $\alpha_r, \beta_r, \gamma_r,$ or $\delta_r,$ the factors being as above stated, viz., definitely known functions of ν, h_0, and m. There is an infinite sequence of such equations for each set of coefficients, one equation corresponding to each value of s, which takes all integral values from 0 to ∞. If we solve them in the same way as for p linear equations in p unknowns, although p is here infinite, we arrive at solutions typified by the equation

$$\alpha_r = \frac{\nabla_r\,(a_{mn})}{\nabla\,(a_{mn})};$$

here a_{mn} denotes the coefficient of α_m in the nth equation of the sequence of equations for the α's (*i.e.*, $s = n$), and $\nabla\,(a_{mn})$ denotes the infinite determinant whose general element is a_{mn}, while $\nabla_r(a_{mn})$ denotes the same determinant with the elements of column $m = r$ all replaced by unity. These determinants are infinite in both directions, covering the whole plane; in each of the equations whence they are derived, m ranges from $-\infty$ to $+\infty$, while the equations of transfer for ΔQ_2 provide a second infinite sequence of equations corresponding to the range of n from -0 to $-\infty$. If we are considering only a simple gas, so that $\nu_2 = 0$, ϕ_2 and ΔQ_2 do not appear, and the determinants reduce to the more ordinary form, covering only a quadrant of the plane.

These general formulæ for the coefficients α, β, γ, δ, complete the determination of the velocity distribution function $f(U, V, W)$. The mean value of any function of U, V, W, can hence be calculated in the form of a linear series of these coefficients. It remains only to add that any such linear series in the α's, β's, γ's, or δ's can readily be transformed into the quotient of an appropriate single determinant by $\nabla(a_{mn})$, $\nabla(b_{mn})$, $\nabla(c_{mn})$, or $\nabla(d_{mn})$ respectively.

PART II.—APPLICATION TO THE THEORY OF THE MEAN-FREE-PATH PHENOMENA.

(1) *Viscosity.*

By I (1) and I (2),the total pressure components $(p_{xx})_0$, $(p_{xy})_0$, are given by

$$(p_{xx})_0 = \nu_1 m_1 \overline{U_1^2} + \nu_2 m_2 \overline{U_2^2} = p_0 - \frac{4}{675} \frac{1}{2h_0} C_0 \left\{ \sum_0^\infty (\nu_1 \gamma_r + \nu_2 \gamma_{-r}) \right\} c_{xx},$$

$$(p_{xy})_0 = \nu_1 m_1 \overline{U_1 V_1} + \nu_2 m_2 \overline{U_2 V_2} = - \frac{4}{675} \frac{1}{2h_0} C_0 \left\{ \sum_0^\infty (\nu_1 \gamma_r + \nu_2 \gamma_{-r}) \right\} c_{xy}.$$

Remembering the significance of c_{xx} and c_{xy}, and comparing these equations with the equations of pressure of a gas whose coefficient of viscosity is κ_{12}, viz., with

$$(p_{xx})_0 = p_0 - \tfrac{2}{3} \kappa_{12} c_{xx}, \qquad (p_{xy})_0 = - \tfrac{2}{3} \kappa_{12} c_{xy},$$

it is clear that the composite gas behaves like a viscous fluid, and that

$$\kappa_{12} = \frac{2}{225} \frac{C_0}{2h_0} \sum_0^\infty (\nu_1 \gamma_r + \nu_2 \gamma_{-r}).$$

(2) *Diffusion.*

From I (3), remembering the significance of ξ_0', it appears that

$$u_0' = \lambda_1 (u_1 - u_0) = - \lambda_2 (u_2 - u_0) = \lambda_1 \lambda_2 (u_1 - u_2)$$

$$= \tfrac{1}{9} A_0 \alpha_0' \left(\frac{1}{2h_0} \frac{\partial \lambda_0'}{\partial x} - X_0' - \frac{m_0'}{\nu_0 m_0} \frac{\partial p_0}{\partial x} \right) + \tfrac{1}{9} B_0 \beta_0' \frac{\partial T_0}{\partial x}.$$

Hence (taking the right-hand terms in order) diffusion is produced by (1) a concentration gradient, or variation in the relative proportions of the constituent gases; (2) by external forces acting unequally per unit mass on the two sets of molecules, and by variations in (3) the total pressure, or (4) temperature of the composite gas. If we write

$$D_{12} = - \tfrac{1}{9} A_0 R T_0 \alpha_0', \quad D_{12}' = D_{12}/p_0, \quad D_p = (m_0'/m_0) D_{12}, \quad D_T = - \tfrac{1}{9} B_0 \beta_0' T_0,$$

then

$$u_0' = - D_{12} \partial \lambda_0' / \partial x + D_{12}' \nu_0 X_0' + D_p \cdot \partial p_0 / p_0 \partial x - D_T \cdot \partial T_0 / T_0 \partial x,$$

and we may call D_{12}, D_{12}', D_p, and D_T respectively the coefficients of diffusion, forced diffusion, pressure diffusion, and thermal diffusion. The definition of D_{12} agrees with that usually given for the coefficient of diffusion. The other coefficients seem to be defined here for the first time.

If, as we have supposed, the molecules m_1 are the heavier, the four coefficients of diffusion are positive. Hence, in the case of pressure diffusion, the heavier gas will tend towards the direction of increasing pressure; in the case of thermal diffusion, the heavier gas will tend towards the direction of decreasing temperature. Evidently both pressure and thermal diffusion will in general take place during the passage of sound through a composite gas such as air, the effects presumably being comparable with those of viscosity and conduction which have been investigated by Stokes, Kirchhoff, and Rayleigh.

(3) *The Transfer of Energy by Conduction, Diffusion, Etc.*

The equation of energy is the equation of transfer of $\frac{1}{2}mC^2$. On combining the separate equations for the two gas-components, the equation of energy for the whole gas, correct to the first order, is found to be

$$
\rho_0 C_v \frac{DT_0}{Dt} + \tfrac{2}{3}\rho_0 C_v T_0 \left(\frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z} \right)
$$

$$
= \frac{1}{J} \Sigma \, v_0 u_0' \left\{ \left(X_1 - m_1 \frac{Du_0}{Dt} \right) - \left(X_2 - m_2 \frac{Du_0}{Dt} \right) \right\}
$$

$$
+ \tfrac{1}{2} \frac{v_0}{J} (m_1 - m_2) c_0^2 \left(\frac{\partial u_0'}{\partial x} + \frac{\partial v_0'}{\partial y} + \frac{\partial w_0'}{\partial z} \right)
$$

$$
+ \frac{\kappa_{12}}{J} \left\{ 2\Sigma \left(\frac{\partial u_0}{\partial x} \right)^2 + \Sigma \left(\frac{\partial w_0}{\partial y} + \frac{\partial v_0}{\partial z} \right)^2 - \tfrac{2}{3} \left(\Sigma \frac{\partial u_0}{\partial x} \right)^2 \right\}
$$

$$
- \frac{1}{J} \Sigma \frac{\partial}{\partial x} \left(\tfrac{1}{2}\rho_1 \overline{U_1 C_1^2} + \tfrac{1}{2}\rho_2 \overline{U_2 C_2^2} \right).
$$

Here C_v is the specific heat at constant volume, and J is Joule's mechanical equivalent of heat. The right-hand terms, it will appear, depend on viscosity, diffusion, and conduction. If we neglect these small effects, the equation may be written

$$
\frac{1}{T_0} \frac{DT_0}{Dt} + \tfrac{2}{3} \left(\frac{\partial u_0}{\partial x} + \frac{\partial v_0}{\partial y} + \frac{\partial w_0}{\partial z} \right) = 0,
$$

or, by the equation of continuity,

$$
\frac{1}{T_0} \frac{DT_0}{Dt} - \tfrac{2}{3} \frac{1}{v_0} \frac{Dv_0}{Dt} = 0, \quad \text{or} \quad \frac{D}{Dt} (T_0 v_0^{-\frac{2}{3}}) = 0, \quad \text{or} \quad \frac{D}{Dt} (p_0 v_0^{-\frac{5}{3}}) = 0.
$$

This is the law of adiabatic expansion of a monatomic gas. The neglected

term, hence give the necessary corrections to this law, which are due to the causes indicated. The left-hand side represents the net rate of increase of energy of molecular agitation, being the increase corresponding to the rising temperature after allowing for the change due to adiabatic alteration of volume. This net rate is analysed as follows, taking the various terms in order :—

(*a*) Work is done on the molecules by the external forces, in the motion of interdiffusion relative to the resultant stream velocity c_0.

(*b*) The variation in the proportions of the molecules m_1 and m_2, due to diffusion, produces a flow of energy of stream-motion c_0, since $\frac{1}{2} m_1 c_0^2$ exceeds $\frac{1}{2} m_2 c_0^2$.

(*c*) The viscous forces cause dissipation of energy, represented by the third term on the right-hand side.

(*d*) The fourth term represents the effect of conduction, together with a hitherto unrecognised term due to diffusion. Supposing, for simplicity, that there is no mass motion, the equation of energy becomes

$$\rho_0 C_v \frac{\partial T_0}{\partial t} = \frac{1}{J} \Sigma \nu_0 u_0' (X_1 - X_2) + \frac{1}{9} \Sigma \frac{\partial}{\partial x} \frac{RT_0}{J} \left[\frac{\overset{\infty}{\underset{1}{\Sigma}} r (\nu_1 \alpha_r + \nu_2 \alpha_{-r})}{\alpha_0'} u_0' \right.$$

$$\left. + \frac{1}{9} B_0 \frac{\partial T_0}{\partial x} \left\{ \overset{\infty}{\underset{1}{\Sigma}} (\nu_1 \beta_r + \nu_2 \beta_{-r}) - \frac{1}{9} \frac{\beta_0'}{\alpha_0'} \overset{\infty}{\underset{1}{\Sigma}} r (\nu_1 \alpha_r + \nu_2 \alpha_{-r}) \right\} \right]$$

on substituting the values of $\overline{U_1 C_1^2}$ and $\overline{U_2 C_2^2}$, and substituting for ξ_0' in terms of u_0' and $\partial T_0 / \partial x$. If, further, there is no diffusion, it reduces to the equation of conduction of heat with thermal conductivity ϑ, viz.,

$$\rho_0 C_v \frac{\partial T_0}{\partial t} = \Sigma \frac{\partial}{\partial x} \left(\vartheta \frac{\partial T_0}{\partial x} \right),$$

where

$$\vartheta = \frac{1}{9} B_0 \frac{RT_0}{J} \left\{ \overset{\infty}{\underset{1}{\Sigma}} (\nu_1 \beta_r + \nu_2 \beta_{-r}) - \frac{\beta_0'}{\alpha_0'} \overset{\infty}{\underset{1}{\Sigma}} r (\nu_1 \alpha_r + \nu_2 \alpha_{-r}) \right\}.$$

It appears also that the motion of interdiffusion is accompanied by a flow of heat proportional to the velocity of diffusion, a process which we shall term the "thermal flux of diffusion." In the absence of conduction, external forces, and mass motion, the equation of energy is thus seen to be

$$\rho_0 C_v \frac{\partial T_0}{\partial x} = \Sigma \frac{\partial}{\partial x} (\mathfrak{D} u_0'),$$

where $\mathfrak{D}$ is defined by

$$\mathfrak{D} = \frac{RT_0}{J} \frac{1}{\alpha_0'} \overset{\infty}{\underset{1}{\Sigma}} r (\nu_1 \alpha_r + \nu_2 \alpha_{-r}),$$

and is called the "specific energy of diffusion."

(4) *The Inequality of the Partial Temperatures.*

In I (3) we found that

$$T_0' = \tfrac{1}{3} D_0 \delta_0' T_0 \, \partial \lambda_0'/\partial t,$$

so that the temperatures of the component gases are unequal by an amount proportional to the rate of change of the ratio of their densities. We will write the equation in the form

$$T_0' = -I_\lambda \, \partial \lambda_0'/\partial t, \qquad I_\lambda \equiv -\tfrac{1}{3} D_0 \delta_0' T_0,$$

I_λ being termed the anisothermal constant of diffusion. Since I_λ is found to be positive, the gas of diminishing relative density is the hotter.

PART III.—DISCUSSION OF THE RESULTS IN VARIOUS SPECIAL CASES.

(1) *Introductory Remarks and Notation.*

The various results arrived at in Part II are complete and perfectly general. To be of service to natural philosophy, however, we must consider their values for selected particular molecular models, and in order to obtain numerical results we must be prepared to make successive approximations to the accurate formulæ. Our usual procedure in this Abstract will be to state the general form of the first approximation, and to determine the correction due to further approximations only for special types of molecule. The types which will be dealt with are (a) point centres of force varying inversely as the nth power of the mutual distance; (b) rigid elastic spheres; and (c) rigid elastic spheres surrounded by a field of attractive force.

The following notation must first be explained, in order that the formulæ of this section may be understood.

$$\mu_1 \equiv m_1/(m_1 + m_2), \quad \mu_2 \equiv m_2/(m_1 + m_2), \quad \mu_{12} \equiv m_1/m_2 = \mu_1/\mu_2 \equiv 1/\mu_{21},$$

$$\phi_{12}{}^k(y) \equiv (2k+1)\{\mu_1\mu_2 h_0(m_1 + m_2)\}^{-\frac{1}{2}} y \int_0^\infty \{1 - P_k(\cos\theta_{12})\} \, p \, dp.$$

Here θ_{12} is the angle through which the relative velocity of two molecules, m_1, m_2, is changed, during an encounter in which p is the distance between their initial or final lines of undisturbed rectilinear motion, and $[(m_1 + m_2)/h_0 m_1 m_2]^{\frac{1}{2}} y$ is the magnitude of their initial or final relative velocity; $P_k(\cos\theta_{12})$ is the Legendre function of $\cos\theta_{12}$, of degree k. If both molecules are of the same kind, m_1 or m_2, the function corresponding to $\phi_{12}{}^k(y)$ is written $\phi_{11}{}^k(y)$ or $\phi_{22}{}^k(y)$. In the next equation,

$$K^k(t) \equiv \frac{4\pi^{-\frac{1}{2}}}{(t+k+\tfrac{1}{2})^{t+k}} \int_0^\infty e^{-y^2} \phi^k(y) \, y^{2(t+k+1)} \, dy,$$

$K^k(t)$ is affected by the same suffixes as the function $\phi^k(y)$ under the

integral sign ; K and ϕ clearly depend upon the molecular model adopted, the various models differing in respect of the dependence of θ_{12} on p and y. Again,

$$k_t \equiv K_{12}{}^1(t)/K_{12}{}^1(0), \qquad k^{(t)} \equiv K^2(t)/K_{12}{}'(0) ;$$

in the latter the suffixes 11, 12, or 22, are to be added to correspond to the suffixes of $K^2(t)$ on the left.

(2) *Particular Molecular Models.*

If the molecules are rigid elastic spheres of radii σ_1, σ_2, it may readily be shown that

$$K_{12}{}^1(0) = 4(\sigma_1+\sigma_2)^2 \left(\frac{m_1+m_2}{h_0\pi m_1 m_2}\right)^{\frac{1}{2}},$$

$$k_t = (t+2)_t/(t+\tfrac{3}{2})_t, \quad k_{11}{}^{(t)} = [2\sigma_1/(\sigma_1+\sigma_2)]^2 k_{12}{}^t, \quad k_{22}{}^{(t)} = [2\sigma_2/(\sigma_1+\sigma_2)]^2 k_{12}{}^t,$$

$$k_{12}{}^{(t)} = \tfrac{5}{3}(t+3)_{t+1}/(t+\tfrac{5}{2})_{t+1}.$$

In these formulæ $(t+2)_t$, or, more generally, r_t, where t but not necessarily r is a positive integer, denotes $r(r-1)\ldots(r-t+1)$.

When the molecules are nth power centres of force, the force at unit distance being $K_{12}m_1m_2$, it may be shown that

$$K_{12}{}^1(0) = \frac{2}{\pi^{3/2}} I_1(n) \left(\frac{h_0 m_1 m_2}{m_1+m_2}\right)^{2/(n-1)-\frac{3}{2}} [K_{12}(m_1+m_2)]^{2/(n-1)} \Gamma\left(3-\frac{2}{n-1}\right),$$

$$k_t = \frac{\Gamma[t+3-2/(n-1)]}{(t+\tfrac{3}{2})_t \, \Gamma[(3-2/(n-1)]},$$

$$k_{12}{}^{(t)} = 5 \frac{\Gamma[t+4-2/(n+1)]}{(t+\tfrac{5}{2})_{t+1} \Gamma[3-2/(n-1)]} \frac{I_2(n)}{I_1(n)},$$

$$k_{11}{}^{(t)} = (K_{11}/K_{12})^{2/(n-1)} k_{12}{}^t, \qquad k_{22}{}^{(t)} = (K_{22}/K_{12})^{2/(n-1)} k_{12}{}^t,$$

where $I_1(n)$, $I_2(n)$, are pure numbers, depending on n only.*

When $n = 5$, so that the molecules are Maxwellian, we may note that $k_t = 1$ for all values of t.

When the molecules are rigid elastic spheres surrounded by a field of attractive force, the latter may be allowed for very approximately by an additional factor $(1+S_{12}/T)$ in $K_{12}{}^1(0)$, a factor

$$\{1+[2/(t+2)]S_{12}/T\}/(1+S_{12}/T)$$

in k_t, and a factor $\{1+[3/(t+3)]S/T\}/(1+S_{12}/T)$ in $k^{(t)}$. Here S_{12}, which is known as Sutherland's constant,† is given by

$$b_{12}{}^2 m_1 m_2/4(m_1+m_2) R,$$

---

* They are the same as the quantities thus denoted in Jeans' 'Dynamical Theory of Gases,' 2nd ed., §§305, *et seq.*

† S_{12} is Sutherland's diffusion constant ; when the gas is simple, S_{12} becomes S_{11}, but Sutherland's constant of viscosity (generally written C) is $\tfrac{2}{3}S_{11}$, or $b_{11}{}^2 m_1/12R$.

where $\frac{1}{2}b_{12}{}^{2}$ is the potential of the force between two molecules m_1, m_2, when in contact; S_{11} and S_{22} are similarly defined, and appear in the numerators of the additional factors in $k_{11}{}^{(t)}$ and $k_{22}{}^{(t)}$.

By putting $m_1 = m_2$, $\nu_2 = 0$, and changing the suffix 2 into 1 throughout, our formulæ for a composite gas reduce to those appropriate to a simple gas. We shall first deal with the latter.

(3) *The Viscosity of a Simple Gas.*

The general first approximation to the coefficient of viscosity κ_{11} of a simple gas is

$$5\,\mathrm{RT}/\pi\,\kappa_{11}{}^{2}\,(0).$$

This result was given and discussed in an earlier memoir,* so that only the correction introduced by further approximations need be considered here.

In the case of rigid elastic spherical molecules, the correction factor is purely numerical, as also in the case of nth power centres of force. Successive approximations to the factor in the former instance are found to be $1\cdot01485$, $1\cdot01588$, $1\cdot01607$, so that $1\cdot016$ times the above result may be taken as exact to well within $\frac{1}{2}$ per cent. For nth power centres of force, similarly, the correction factor is found to have the values $1\cdot000$, $1\cdot004$, $1\cdot007$, $1\cdot011$, $1\cdot016$, corresponding to the typical values 5, 9, 15, 25 and infinity for n.

In the case of rigid elastic attracting molecules, the correction factor varies very slightly with temperature. Typical values, corresponding to the values ∞, 5, 3, 1, $0\cdot4$, $0\cdot2$, $0\cdot1$, 0 for S/T, are respectively $1\cdot016$, $1\cdot010$, $1\cdot006$, $1\cdot000$, $1\cdot004$, $1\cdot014$, and $1\cdot015$. Thus, in all cases, the first approximation is exceedingly close to the exact value.

(4) *The Thermal Conductivity ϑ_{11} of a Simple Gas.*

A first approximation leads to the result

$$\frac{5}{2}\,\kappa_{11}\,\mathrm{C}_v$$

as given in the earlier memoir just cited. As in the case of viscosity, the correction consists of a numerical factor to be applied to the above result; this factor is very nearly unity, being $1\cdot010$ for rigid elastic spheres, and for nth power centres of force varying from $1\cdot000$ for $n = 5$, through the values $1\cdot003$, $1\cdot006$, $1\cdot007$ for $n = 9$, 15, and 25, to $1\cdot010$ for $n = \infty$. Similarly for attracting spheres, as S/T takes the values ∞, 5, 3, 1, $0\cdot4$, $0\cdot2$, $0\cdot1$, 0, the factor is found to equal $1\cdot022$, $1\cdot007$, $1\cdot003$, $1\cdot000$, $1\cdot002$, $1\cdot003$, $1\cdot004$, and $1\cdot010$ respectively. The corrections to the first approximation are

* 'Phil. Trans.,' A, vol. 211, pp. 433–483, §§17, 20 (1911).

hardly within the present experimental powers of measurement, and the simple formula $\frac{1}{2}\kappa_{11}C_v$ agrees well with the observed values for argon, helium, and neon.

(5) *The Coefficient of Diffusion* D_{12}.

The general first approximation to D_{12} is

$$3\left(m_1 + m_2\right) RT / 2\pi\nu_0 m_1 m_2 K_{12}{}^1\left(0\right).$$

This result was first obtained by Langevin, and subsequently, independently, in the earlier memoir by the present author, already cited. Like the first approximations also to κ_{11}, ϑ_{11}, and κ_{12}, it is an exact formula in the case of Maxwellian molecules, and in no other. Maxwell obtained this expression for D_{12} in his own special case, though without a rigorous proof; his method when applied to other cases (as by the authors named) leads only to the above first approximation, the error of which is in some cases considerable. We shall write the correction factor introduced on a second approximation in the form $1/(1 - \epsilon_0)$. Before considering the value of ϵ_0 we shall examine some particular cases of our formulæ which throw light on the accuracy of a second approximation in general.

When the mass and size of the molecules m_2 are negligible compared with those of m_1, an exact solution for D_{12} is obtainable, as Lorentz first showed. The first few approximations to the correction factor in this case, when the molecules are rigid elastic spheres, are found to be 1·083, 1·107, 1·117, converging to the value $32/9\pi$ or 1·132. If the molecules are nth power centres of force, the correction factor is equal to

$$\frac{16}{9}\left(1 + \frac{2}{n-1}\right)\frac{2}{n-1}\left(1 - \frac{2}{n-1}\right)\left(2 - \frac{2}{n-1}\right)\frac{1}{\sin\left[2\pi/(n-1)\right]},$$

which, when n is 5, 9, 13, 17, ∞, has the respective values 1·000, 1·031, 1·056, 1·072, 1·132. These results agree with Lorentz's theory, and show that in this case, at any rate, the first approximation to D_{12} is seriously in error.

The next simplest case of a general character with which we can deal is that in which the molecules m_1, m_2 are identical in dynamical properties (*e.g.*, mass, size, force), as, for instance, in the diffusion of a gas into itself. Hence we shall in this case write D_{11} for D_{12}. The correction factor is found to depend only on the nature of the molecule; its values for nth power centres of force, when n equals 5, 9, 17, or ∞, are respectively 1·000, 1·004, 1·008, or 1·015, and the last value also corresponds to rigid spherical molecules. These are only first approximations, but would not be altered by further approximations by more than 0·001 or 0·002. The complete formula for rigid spherical molecules is

$$0{\cdot}1520/\nu_1\left(2\sigma_1\right)^2\left(h_1 m_1\right)^{1/2}.$$

The correction factor in this case had been previously calculated approximately by Pidduck, who obtained 0.151 (given thus to three decimal places only) in place of 0.1520 as above.

For the same type of molecule, we also have $D_{11} = 1.200 \, \kappa_{11}/\rho_1$, which may be compared with an approximate result obtained by Jeans, using the "mean-free-path" method, viz., $D_{11} = 1.34 \, \kappa_{11}/\rho_1$. For other types of molecule, D_{11} is a different multiple of κ_{11}/ρ_1.

(6) *Variation of D_{12} with the Ratio of Mixture ν_1/ν_2.*

The above first approximation to D_{12}, it may be noticed, depends only on $\nu_1 + \nu_2$, and not at all on the ratio $\nu_1 : \nu_2$. Meyer disputed the independence of D_{12} on the ratio of mixture, and developed a theory predicting considerable changes of D_{12} as ν_1/ν_2 was varied. Experimental results showed a small variation of D_{12}, but much less than Meyer's formula alleged. This cast suspicion on both Maxwell's and Meyer's theories; it now appears that the former was correct, but failed to represent the facts because of the unsuitability of the molecular model. A Maxwellian gas is the only one for which D_{12} is independent of ν_1/ν_2. The correction factor to the above approximate formula is in every other case a function of ν_1/ν_2.

We shall consider only the approximation $1/(1-\epsilon_0)$ to the correction factor; this is very nearly exact. We find that

$$\epsilon_0 = (k_1 - 1)^2 \frac{b_1 \nu_1^2 + 2 \, b_{12} \nu_1 \nu_2 + b_2 \nu_2^2}{d_1 \nu_1^2 + 2 \, d_{12} \nu_1 \nu_2 + d_2 \nu_2^2},$$

where

$$b_1 = 2\mu_1\mu_{12}k_{11}^0, \quad b_2 = 2\mu_2\mu_{12}k_{22}^0, \quad 2b_{12} = 30\,(1-4\mu_1\mu_2) + 8\mu_1\mu_2 k_{12}^0,$$

$$d_1 = \frac{1}{\mu_2} k_{11}^0 \left\{ \tfrac{12}{5}(1-2\mu_1\mu_2) + \tfrac{16}{25}\mu_1\mu_2 k_{12}^0 - 2\left(\tfrac{1}{5} + 2k_1 - \tfrac{7}{5}k_2\right)\mu_1^2 \right\},$$

$$2d_{12} = \frac{4}{25}\frac{1}{\mu_1\mu_2} k_{11}^0 k_{22}^0 + \tfrac{6}{5}(1-4\mu_1\mu_2)\left(1-2k_1+\tfrac{7}{5}k_2\right) + 8\mu_1\mu_2 k_{12}^0\left(\tfrac{11}{5} - 2k_1 + \tfrac{7}{5}k_2\right),$$

and d_2 is obtainable from d_1 by interchanging the suffixes 1 and 2.

The behaviour of ϵ_0 with change of ν_1/ν_2 is easily studied when the molecules are rigid elastic spheres. In this case (remembering the convention $m_1 \gg m_2$) it appears that b_1/d_1 exceeds b_2/d_2, and that b_{12}/d_{12} exceeds b_2/d_2. Further, if

$$\left\{ \frac{4\sigma_1\sigma_2}{(\sigma_1+\sigma_2)^2} \right\}^2 \gg \frac{1}{4}\frac{\mu_2^3}{\mu_1}(1 + 80\mu_2 - 100\mu_1\mu_2),$$

we have $b_1/d_1 \gg b_{12}/d_{12} \gg b_2/d_2$; the signs of equality correspond to the case $m_1 = m_2$, $\sigma_1 = \sigma_2$, as in self diffusion. This indicates why D_{11} does not depend on ν_1/ν_2. In the general case, if the above condition is fulfilled,

ϵ_0 and $1/(1-\epsilon_0)$ steadily decrease, as the proportion of molecules m_2 is increased, while, if it is not fulfilled, ϵ_0 and $1/(1-\epsilon_0)$ (and consequently also D_{12}) first increases and then decreases, as λ_2 increases from 0 to 1. Clearly, the more equal the molecular masses, the more equal also must be the molecular radii, in order that the above condition may be fulfilled.

As regards the magnitude of the correction factor, it is greater the more unequal the diameters and masses of the molecules, reaching a maximum of $32/9\pi$, or 1·132, when m_1/m_2 and σ_1/σ_2 are infinite. This is for rigid spherical molecules: for other types the range is less, shrinking to zero in the case of Maxwellian molecules. In other cases the factor appears always to exceed unity.

The magnitude of the variation in ordinary cases, and the comparison of experiment with theory, may be gauged from the following Table* ; the theoretical values of D_{12} are so calculated as to make their mean agree with the mean of the experimental values, so that the theory is concerned only with the variations from the mean. The molecules are assumed to be rigid spheres, though a less simple model might prove still better.

Gases.	$\lambda_1 = \dfrac{\nu_1}{\nu_1 + \nu_2}$	Correction factor.	D_{12}.	
			Observed.	Calculated.
Argon and helium	0·273	1·050	0·244	0·248
	0·315	1·056	0·250	0·250
	0·377	1·063	0·250	0·251
	0·500	1·073	0·254	0·254
	0·677	1·087	0·256	0·257
	0·763	1·094	0·263	0·259
Oxygen and hydrogen	0·25	1·050	0·276	0·276
	0·5	1·073	0·280	0·282
	0·75	1·097	0·289	0·289

It may be added that Kuenen† has improved Meyer's theory of D_{12} by taking persistence of velocities into account, and has thus much reduced Meyer's predicted variations with ν_1/ν_2, though they still remain twice or thrice as great as the observed changes.

* The observed data were obtained in the Halle Laboratory, under Prof. Dorn, by Schmidt, Deutsch, Jackmann, and Lonius ('Ann. d. Phys.,' vol. 29, p. 664, 1909).

† Kuenen, Supp. 8 to 'Leiden Phys. Comm.,' January, 1913.

(7) *Thermal and Pressure Diffusion.*

The first approximation to the coefficient of thermal diffusion D_T is

$$\frac{3\,(m_1+m_2)\,\mathrm{RT}}{2\,\pi\nu_0 m_1 m_2 \mathrm{K}_{12}{}^1\,(0)}\,\frac{(k_1-1)\,\epsilon_1}{\nu_0\Delta_1},$$

where

$$\epsilon_1 = 30\,(\nu_1\mu_2+\nu_2\mu_1)\,(\mu_1-\mu_2)-8\mu_1\mu_2 k_{12}{}^0\,(\nu_1-\nu_2)+2\,(\nu_1\mu_{12}k_{11}{}^0-\nu_2\mu_{21}k_{22}{}^0),$$

and

$$\Delta_1 = (1/\nu_1\nu_2)\left\{(d_1\nu_1{}^2+2d_{12}\nu_1\nu_2+d_2\nu_2{}^2)-(k_1-1)^2\,(b_1\nu_1{}^2+2b_{12}\nu_1\nu_2+b_2\nu_2{}^2)\right\}.$$

In the case of Maxwellian molecules D_T vanishes (as also every approximation to it, as here, since $k_1 = 1$ for such a gas); like the variation of D_{12} with ν_1/ν_2, thermal diffusion is a phenomenon which wholly disappears in this alone out of all typical gases, so that the model is far from suitable physically, whatever its mathematical advantages.

Thermal diffusion depends essentially on a difference of mass and structure between the molecules m_1, m_2; if $m_1 = m_2$ and $k_{11}{}^0 = k_{22}{}^0$, etc., D_T vanishes, as the above first approximation also suggests. The more unequal the molecules, the greater is D_T. Considering elastic spherical molecules, if $\sigma_1 = \sigma_2$ but m_1/m_2 is very large, D_T reduces approximately to

$$D_{12}\,.\,15\lambda_1\lambda_2/\,(39+\lambda_2)$$

(thus if $\lambda_1 = \lambda_2 = \tfrac{1}{2}$, $D_T = 0{\cdot}095\,D_{12}$ nearly). When both m_1/m_2 and σ_1/σ_2 are very large (Lorentz's case)

$$D_T = \frac{3\lambda_2}{16\nu_0\,(\sigma_1+\sigma_2)^2\,(h\pi m_2)^{1/2}}\,\frac{D_1{}'}{D'},$$

where first, second, and third approximations to the numerical factor $D_1{}'/D'$ give $0{\cdot}417$, $0{\cdot}494$, $0{\cdot}524$, converging to $0{\cdot}58$ nearly—this also illustrates the degree of correction introduced on further approximations after the first, although the error of the latter is at its maximum for this specially unequal molecular pair; the above formula is, moreover, true only so long as λ_2 is not too nearly equal to 1, since D_T vanishes with $\lambda_1\lambda_2$ always. If $\lambda_1 = \lambda_2 = \tfrac{1}{2}$, we get $D_T = 0{\cdot}26\,D_{12}$ nearly, which may be compared with the former case when $\sigma_1 = \sigma_2$, as illustrating the effect of the inequality between the molecular diameters when m_1/m_2 is very large.

Pressure diffusion likewise depends on the inequality of the molecules (of their masses only, however). Thus

$$D_p = D_{12}\,.\,\lambda_1\lambda_2\,(m_1-m_2)/(\lambda_1 m_1+\lambda_2 m_2).$$

The following Table illustrates the relative magnitudes of D_{12}, D_T and D_p for a few typical gas-pairs (rigid elastic spherical molecules being assumed):—

Ratio of mixture, $\nu_1 : \nu_2$.	A–He $m_1/m_2 = 9 \cdot 8$ $\sigma_1/\sigma_2 = 1 \cdot 7$.			O–H $m_1/m_2 = 16$ $\sigma_1/\sigma_2 = 1 \cdot 3$.			O–N $m_1/m_2 = 1 \cdot 1$ $\sigma_1/\sigma_2 = 1 \cdot 0$.		
	D_T/D_{12}.	D_p/D_{12}.	D_p/D_T.	D_T/D_{12}.	D_p/D_{12}.	D_p/D_T.	D_T/D_{12}.	D_p/D_{12}.	D_p/D_T.
1 : 3	0·133	0·513	3·9	0·122	0·592	4·8	0·008	0·026	3·2
1 : 1	0·132	0·408	3·1	0·128	0·441	3·4	0·010	0·033	3·3
3 : 1	0·079	0·166	2·1	0·079	0·230	2·9	0·007	0·024	3·4

In this connection we may also remark on the steady state of a gas without diffusion, under the influence of (*a*) external forces or (*b*) of a permanently maintained non-uniform temperature distribution. In the former case the pressure will, of course, be non-uniform. The equations of diffusion show that a permanently non-uniform composition will thus be set up, depending in case (*a*) on the ratio D_{12}'/D_{12} or D_p/D_{12}, and in (*b*) on D_T/D_{12}. Both cases are exemplified in the upper strata of the atmosphere, above the region of convection, and in a future note the effect of temperature gradient on atmospheric constitution will be indicated in detail; it is less, however, than the effect of the diminishing pressure. The influence of non-uniform temperature on composition has been verified experimentally, the proportions of two gases being found to differ in two bulbs kept at different temperatures and with an open connection between them; a preliminary account of these experiments will appear shortly. The magnitude of the effect is easily indicated by an example; if argon and helium, or oxygen and hydrogen, are the gases, mixed in originally equal proportions, and the hot bulb is kept at 100° C. and the cold at 0° C., the heavier gas will concentrate slightly in the cold bulb, 52 per cent. of it to 48 per cent. of the lighter gas, instead of the original 50 per cent. to 50 per cent., and *vice versâ* at the hot bulb.

(8) *Viscosity and Conduction in Mixed Gases.*

The formulæ for κ_{12} and ϑ_{12} in mixed gases are very complicated. A first approximation to κ_{12} agrees with that given in my first memoir, but the first approximation to ϑ_{12} was there given wrongly, since, in deriving it, it was assumed that conduction could take place in a uniform gas without diffusion, which we have just seen to be impossible. The correct formula is given in the second memoir here abstracted, but will not be reproduced in this place.

(9) *Inequality of the Temperatures of the Component Gases.*

This phenomenon has been shown to depend on $\partial\lambda_0'/\partial t$, or the time rate of variation of the relative proportions of the component gases. The following

example will illustrate its order of magnitude. Consider a gas composed initially of equal numbers of molecules which are similar to one another in mass and other dynamical properties (since the phenomenon does not, like thermal diffusion, depend on molecular differences, this assumption may legitimately be made, in order to obtain a simple numerical illustration). We will suppose that the gas is at normal temperature and pressure, and that the molecules are similar in mass and size to oxygen molecules, though differing from one another in some other respects. Then if the proportions are changing at such a rate that at the end of one second there will be 51 per cent. of one component to 49 per cent. of the other, a temperature difference of about one thousand-millionth of a degree Centigrade will be set up, the hotter gas being that which is in diminishing ratio. Thus equipartition of energy is disturbed only by a negligible amount even in this rather extreme case.

On the Mechanical Relations of the Energy of Magnetisation.

By G. H. Livens, The University, Sheffield.

1. There still appears to be some uncertainty in the expression for the total energy of a magnetic field, and the mode of its separation into its fundamental constituents, as belonging to the æther and the matter. This is chiefly due to certain discrepancies of sign which exist in the results of the theory in its statical and dynamical aspects. In the statical theory the energy is usually made to appear as though distributed over the field with the density $\mu H^2/8\pi$, which corresponds to an æthereal density of amount $H^2/8\pi$, but in the dynamical theory the same expressions are obtained with opposite signs. In some quarters it is considered that there are difficulties of a fundamental nature involved in any attempt to remove this discrepancy, and several authors[*] have tried to construct a more consistent theory on a new basis.

The object of the present note is mainly to prove that it is possible to interpret the older and more usual form of the theory in a perfectly logical and consistent manner, so that the aforementioned discrepancy does not

* *Cf.* 'Encyclopädie der mathematischen Wissenschaften,' vol. 5, Art. 15, " Electrostatik u. Magnetostatik " (R. Gans), p. 338, where full references are given.